Single Particle Studies of Cation-Exchange Rates in Packed Beds: Barium Ion-Sodium Ion System

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The use of numerical methods and high-speed computers for the design of packed-bed ion exchange units can obviate the rather severe limitations imposed by complicated mathematics on the existing design methods for these units. Before such numerical methods can be established and used, however, further fundamental studies of the exchange process in packed beds are necessary, both to establish the correct mathematical models and to provide specific data and generalized correlations for rate and other necessary design constants. The present work is part of a basic study of ion-exchange rates in packed beds and has as a primary objective to obtain pertinent rate constants for the exchange reaction $Ba^{++} + 2Na\,R \rightleftarrows 2Na^{+} + BaR_2$.

For the usual porous ion-exchange particles the rate of ion exchange is controlled by the resistance to mass transfer between the external fluid and the exchanger surface and/or the resistance to mass transfer within the exchanger (*2, 17*). Equilibrium is assumed to exist at the exchanger-fluid interface. This situation is similar to that in many mass transfer processes of chemical engineering, and most of the more recent studies have viewed the transfer between the bulk fluid and exchanger surface (often called *liquid-film diffusion*) in packed beds as a quasi-stationary state representable by

$$\frac{dq}{dt} = k_{LS}\,(c - \bar{c}) \qquad (1)$$

Adamson and Grossman (*1*) have pointed out that for exchange of ions with different diffusivities, the total solution normality should not be the same at the interface as in the bulk of the solution (the effect of this change on $\bar{c}$ has often been overlooked in subsequent studies); and Schlögl and Helfferich (*16*) have shown that theoretically the electrical forces resulting from counterexchange of ions with different diffusivities will affect both the total solution normality at the interface and the rate of mass transfer between the bulk liquid and the exchanger surface.

The rate of mass transfer within the ion-exchange particle is considered a diffusional process and has generally been described either by Fick's second law (*2, 17, 19, 20*) or by simpler approximations which often employ the assumption of a linear concentration gradient within the particle (*6, 9*). The internal diffusivity appearing in such equations has usually been taken as a constant characteristic of the exchange system. However, Helfferich and co-workers (*11, 15*) and Gilliland et al. (*7*) have shown that for the exchange of ions having different mobilities, the electrical field induced by their counterdiffusion results in a varying value for the diffusivity as defined by Fick's law. This interdiffusion coefficient is a function of the exchanger composition at the point in question and the self-diffusivities (within the exchanger) and valences of the exchanging ions.

In packed beds, control of the exchange rate by the rate of mass transfer between the solution and particle surface is favored by dilute solutions, favorable equilibrium, low flow rates, and small particle size (*2*). The opposites of these conditions tend to make internal diffusion the rate-controlling step.

EXPERIMENTAL PROCEDURES

Previous rate studies of ion exchange have principally employed deep packed beds, differential beds, or stirred-vessel batch systems. The first of these methods is lengthy, and the experimental results are difficult to interpret in terms of the complex mechanisms which may be determining the rate of exchange. The second method poses experimental difficulties for studies with concentrated solutions (*3*); and the stirred-vessel technique does not duplicate the conditions found in a packed bed. Accordingly the single-particle method (*3*) was used for the present study. In this method, a single particle of exchanger charged with a cation species tagged by a radioactive tracer is placed in a bed of similarly sized glass beads. A solution of known concentration of a second cation is passed through the bed at a desired flow rate, and the rate of exchange is determined directly by continuous measurement of the residual radioactivity on the particle. The actual amount of exchange occurring is so small that the composition of the external solution is essentially unchanged. The surface area of the particle can be determined from diameter measurements.

For the exchange system of the study it was desired that the exchanging cations have different valences (rate data are scarcer for this type of exchange) complex-ion formation and hydrolysis be absent, safe radioactive isotopes of sufficiently long half-life and low cost be available for both cations, and the system be combinative with another binary system already under study to form a system satisfactory for multi-component ion-exchange studies. The barium ion-sodium ion system with chlorine ion as the coupling ion was chosen as satisfying these requirements. Barium-133 and sodium-22 were used as the tracer ions. Rate studies were made for both directions of exchange with N/100 and 2N solutions. The N/100 runs were intended primarily to study operation wherein transfer between the bulk liquid and particle surface controls the exchange rate; the 2N runs were to study the diffusional process inside the particle.

Dowex 50W-X8 cation exchange resin was selected as being representative of modern, commercially available exchangers. Previous studies (*5, 8, 12*) have shown this exchanger to have excellent homogeneity of ion-exchange properties. A small batch of the exchanger was pretreated by several alternate conversions to the sodium and barium forms. Individual particles were selected on the basis of spherical shape, freedom from flaws, and desired size by examination under the microscope. Their diameters were measured

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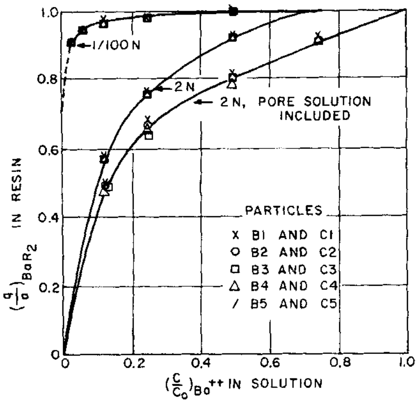

Fig. 1. Exchange isotherms.

by use of a micrometer eyepiece. At the conclusion of the experimental work, the particles were dried at 120°C. and weighed on a microbalance having a sensitivity of 0.002 mg. The properties of the particles used are given in Table 1.

For an experimental rate determination, a particle in barium or sodium form, containing enough tracer to provide a satisfactory count, was washed thoroughly with distilled water and carefully placed in the center of a 40-mm. high bed of 1-mm. glass beads in a 10-mm. I.D. glass tube. A fritted glass disk sintered in the tube supported the bed during preparation and the finished bed was held in place at the other end by a plug of glass wool which also served as a distributor during a run. The entire bed unit was then attached to the feed system with the glass disk uppermost. The tube was filled with distilled water before bed construction, and care was taken to keep the bed and lines free of air during assembly of the system and during operation. All runs were made upflow, and the feed system was so arranged that by quickly opening a stopcock, a predetermined flow rate through the bed could be obtained almost instantaneously. The flow rate was verified during a run by a flowmeter and direct measurement of the effluent.

The feed solution contained only a single cation species and no tracer. The radioactivity of the exchanger particle with the bed in operating position was measured for several minutes before the start of a run and throughout the course of the run. The background count was measured both before and after the run. With sodium-22 tracer, a Geiger-Mueller counter, rate meter and continuous recorder were used to measure the particle radioactivity. With barium-133 a scintillation detector and scaler were used in place of the Geiger-Mueller counter. The somewhat wavy curve from the recorder, caused by the randomness of the decay process, was easily smoothed by eye. It is estimated that in general the count read from the curve was correct to within at least 1% of the initial count for the scintillation detector and 2% for the Geiger-Mueller counter.

The exchange capacity and the equilibrium curves were obtained for each of the particles of the study both to verify the homogeneity of the particles and for use in the rate study. For this portion of the work, 2N tagged sodium chloride and barium chloride solutions were accurately prepared, and equilibrating solutions were made by mixing the proper amounts of one or the other of these with a nontagged solution of the other cation. To determine a particular equilibrium, a particle was equilibrated with successive small batches of the desired composition solution until the count of the particle became constant. The particle was left in each successive batch for 8 to 12 hr., during which time the container was kept on a rotating tilted turntable or a vibratory shaker. The particle was dried with a cotton swab and filter paper upon removal from solution and placed in 1 ml. of distilled water in a standard vial for counting. Immediately after the equilibrium count was measured (a matter of minutes), the particle was rinsed with running distilled water for several hours to elute the pore solution and was recounted. These counts were compared with the count from a very accurately measured 1 ml. sample of known strength of the appropriate tagged cation to give directly the quantity of that cation on the particle. Corrections were made for background, geometry, and decay. The capacity of the particle was determined simply by using an equilibrating solution containing only a single cation. A Geiger-Mueller counter and scaler were used for the sodium-22 counts and a scintillation detector and scaler for the barium-133 counts. Capacity counts were reproducible to within ±1% and equilibrium counts to within ±2.5% at the lowest counting levels.

DISCUSSION OF EQUILIBRIUM RESULTS

The capacity and equilibrium data obtained for the exchanger are given in Table 1 and Figures 1 and 2.[*] Though these results are presented primarily to aid with subsequent discussion of the rate studies, various aspects of them warrant comment per se.

The homogeneity in ion-exchange properties of the particles used in the study is well indicated by their specific capacities in Table 1 and the agreement in equilibrium compositions in Figure 1. The agreement is least satisfactory for the 2N curve with pore solution included, probably because of the crude method (see procedure) used to remove surplus equilibration solution from the outside of the particles.

The ionic content of the liquid in the pores of the particle (pore solution) was negligible for N/100 equilibrating solutions. However, inclusion of the pore solution appreciably affects the 2N curve, as is shown in Figure 1. The lower of the 2N curves is for exchanger compositions before washing of the particles; the upper 2N curve was obtained after elution of the pore solution. The amount of barium eluted from the pores for the 2N case is shown in Figure 2 and represents at higher c/c_o's a sizeable fraction of the exchange capacity. As pointed out for a similar system (*18*), it is probable that for the lower range of c/c_o in Figure 2, the pore solution barium content shown is lower than the true equilibrium value because of further barium take-up by the exchanger during washing.

Equilibrium distribution coefficients defined by Equation (2) were determined for the data of Figure 1 with the pore solution included in the exchanger composition:

$$\frac{\left(\frac{q}{a}\right)\mathrm{Ba}R_2}{\left[1-\left(\frac{q}{a}\right)\mathrm{Ba}R_2\right]^2} = \left(\frac{Ka}{c_o}\right)\frac{\left(\frac{c}{c_o}\right)\mathrm{Ba}^{++}}{\left[1-\left(\frac{c}{c_o}\right)\mathrm{Ba}^{++}\right]^2} \qquad (2)$$

The value of a on the right side of the equation was taken as 5.1 meq./(g. dry hydrogen form of the resin) for both concentrations. The distribution coefficients obtained were $K_{2N} = 4.6$ g./ml. and $K_{N/100} = 8.4$ g./ml. The K values for individual points differ as much as 20% from the above 2N value and 50% for the N/100 value. For the most part these deviations stem from the effect of very slight errors in q/a on K at high values of q/a. The predicted curves obtained with the K values given agree most excellently with the corresponding experimental curves. The change in K with concentration is in qualitative agreement with changes in activity coefficients for the external solution components (*13*).

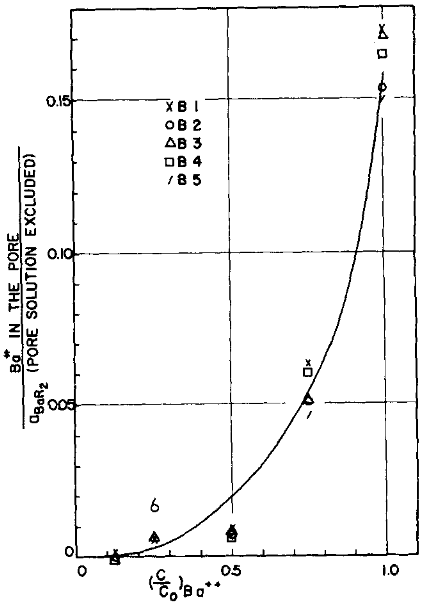

Fig. 2. Apparent barium content of pore solution.

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[*] A more complete compilation of the experimental data for both the equilibrium and rate studies, as well as further details of the experimental procedures, are given in reference *13*.

RATE STUDIES WITH N/100 SOLUTIONS

The N/100 runs were primarily to obtain mass transfer coefficients for the ionic transfer between the bulk of the solution and the surface of the exchanger particle. The experimental results are given in Figures 3 and 4. Increase of exchange rate with increased flow rate through the bed may be noted from both figures and indicates that mass transfer across the liquid film plays an important part in determining the exchange rate. Runs A2 and A3 of Figure 3 are duplicate runs to show the reproducibility of the experimental data.

Forward Reaction (barium replacing sodium)

For N/100 barium chloride external solution, the equilibrium is essentially irreversible in favor of the barium form of the resin, until the particle is almost saturated with barium (see Figure 1). Since no sodium was present in the feed solution for the forward reaction runs, Equation (1) can be written, for the first portion of a run, as

$$\frac{d(q/a)_{Ba}}{dt} = \frac{-d(q/a)_{Na}}{dt} = \frac{(k_L)_{Ba}\, s\, c_o}{a} \qquad (3)$$

Equation (3) indicates that for the case under consideration, $(q/a)_{Ba}$ should vary linearly with time. In Figure 3 this is seen to be true for the earlier portion of particle saturation before accumulation of barium within the particle causes internal diffusion to have an appreciable effect on the rate. As would be expected, the liquid film is rate controlling for a decreasing fraction of particle saturation as the flow rate is increased.

The $(k_L)_{Ba}$ values obtained by Equation (3) are tabulated in Table 2. The value for s, the particle surface, was taken at the average of the diameters in the sodium and barium forms (Table 1). Figure 5 is a correlation of the $(k_L)_{Ba}$ values by the J-factor method of Dryden (4), where

$$J_D = \frac{k_L \epsilon}{V'}\left(\frac{\mu}{\rho D}\right)^{0.58} \qquad N_{Re} = \frac{d_p V' \rho}{\mu \epsilon} \qquad (4)$$

In Figure 5, the barium data lie between the curves of Dryden for liquid-phase mass transfer coefficients and Selke et al. (17) for ion exchange and show essentially the same effect of velocity on k_L. To evaluate the Schmidt and Reynolds numbers in Equation (4), the viscosity and density of water at 25°C. were used, the bed void fraction ϵ was taken as 0.4, and the diffusivity of the barium ion was taken as (1.0) (10^{-5}) sq. cm./sec. This last value is the average of the interdiffusivity coefficients for barium diffusing counter to sodium, with chloride as the mobile anion, as calculated by the method of Gilliland et al. (7) for the two extremal cases of equal normality gradients for the exchanging ions and of normality gradients proportional to self-diffusivities [D = (0.95)(10^{-5}) and (1.05)(10^{-5}) sq. cm./sec. respectively]. The ionic self-diffusivities of sodium and barium used were respectively (1.35) (10^{-5}) sq. cm./sec. (*14*) and (0.83)(10^{-5}) sq. cm./sec. (*21*). It must be recognized that the values chosen for d_p, ϵ, and D can appreciably affect the location of the correlating curve.

TABLE 1. PROPERTIES OF EXCHANGER PARTICLES

Particle	Capacity,* μeq Ba	Capacity,* μeq Na	Weight, mg. (dry H form)	Specific capacity, meq./g. dry H form	Diameter, mm.† HR in H_2O	Diameter, mm.† NaR in H_2O	Diameter, mm.† BaR_2 in H_2O	Diameter, mm.† NaR in 2N NaCl	Diameter, mm.† BaR_2 in 2N $BaCl_2$
B1	2.69	2.73	0.531	5.10	1.26	1.23	1.15	—	—
B2	2.00	1.98	—	—	1.13	1.08	1.04	—	—
B3	1.95	1.95	0.385	5.07	1.12	1.06	1.02	1.05	1.02
B4	1.74	1.68	0.348	5.00	1.08	1.06	0.99	1.02	0.98
B5	1.83	—	0.359	5.09	1.10	1.05	1.00	—	—
C1	2.68	—	—	—	—	1.21	—	—	—
C2	2.10	—	0.409	5.14	—	1.11	1.04	—	—
C3	2.35	—	0.461	5.11	—	1.16	1.09	—	—
C4	2.44	—	0.478	5.11	—	1.17	1.10	—	—
C5	1.83	—	0.359	5.19	—	1.08	1.00	—	—

* After washing.

† Swelling factors based on diameter in H form as 1.00:
NaR in H_2O: 0.964 BaR_2 in H_2O: 0.906
NaR in 2N NaCl: 0.940 BaR_2 in 2N $BaCl_2$: 0.904

Reverse Reaction (sodium replacing barium)

The particle saturation rates were much lower for the reverse reaction than for the forward reaction as may be readily noted from comparison of the data in Figures 3 and 4. Primarily this results from the favorability of the equilibrium for the barium form of the exchanger and the consequent low driving forces for the sodium ions going from the solution to the exchanger.

Determination of liquid-film mass transfer coefficients for the reverse reaction was more difficult than for the forward reaction since the composition of the liquid at the interface could not be determined readily. The usual liquid-film mass transfer coefficient for the reverse reaction is defined by

$$\frac{d(q/a)_{Na}}{dt} = \frac{(k_L)_{Na} s}{a}\left(c_{Na} - \bar{c}_{Na}\right) \qquad (5)$$

where $c_{Na} = c_o$ for the experimental technique used and $\bar{c}_{Na}$ is in equilibrium with $\bar{q}_{Na}$. Material balance considerations dictate that

$$(k_L)_{Na}(c_o - \bar{c}_{Na}) = -(k_L)_{Ba}(c_{Ba} - \bar{c}_{Ba}) = (k_L)_{Ba}\bar{c}_{Ba} \qquad (6)$$

Since $(k_L)_{Na}$ will ordinarily not be the same as $(k_L)_{Ba}$ because of the different diffusivities of sodium and barium, the concentration gradients for these two ions will differ, and the total solution normality at the interface will not equal c_o. To minimize the complications this change in total solution normality introduces into the calculation and correlation of the liquid-film mass transfer coefficient, it was found desirable to work with the coefficient defined by

$$\frac{d(q/a)_{Ba}}{dt} = \frac{-(k_L)_{Ba}\, s\, \bar{c}_{Ba}}{a} \qquad (7)$$

The k_L's of Equations (5) and (7) should be related by $(k_L)_{Na}/(k_L)_{Ba} = (D_{Na}/D_{Ba})^{0.58}$ [see Equation (4)] or a similar relationship.

For a constant mass transfer coefficient, Equation (7) may be rewritten in integrated form as

$$-\int_{q/a=1}^{q/a} \frac{d(q/a)_{Ba}}{\bar{c}_{Ba}/c_o} = \frac{(k_L)_{Ba}\, c_o\, s}{a}\, t \qquad (8)$$

If the internal diffusion has no effect upon the exchange rate, $\bar{c}_{Ba}$ is in equilibrium with q_{Ba}, and the integral is simply a function of $(q/a)_{Ba}$. For small differences between the total solution normality at the interface and

TABLE 2. MASS TRANSFER COEFFICIENTS

N/100 $BaCl_2$ runs				
Run	A-1	A-2 and A-3	A-5	A-6
V', cm./sec.	0.42	2.70	5.25	7.80
$(k_L)_{Ba}$, cm./sec.	0.00517	0.00945	0.0145	0.0192
N_{Re}	12.2	78.1	152	226
J_D*	0.234	0.0667	0.0566	0.0469
N/100 NaCl runs				
Run	C-4	C-3	C-1	C-2
V', cm./sec.	0.133	2.11	4.00	10.9
$(K_L)_{Ba}$, cm./sec.	0.001334	0.00335	0.00375	0.00731
N_{Re}	3.86	61.2	116	316
J_D	0.231	0.0365	0.0216	0.0155

* The J_D values for N/100 barium chloride runs given in reference *13* (and subsequent discussion pertinent to those J_D values) were based on a different (higher) value of $D_{Ba^{++}}$.

c_o, the integral can be evaluated graphically from the equilibrium curve for c_o. However, even without these restrictions, the integral may still be evaluated in the same manner, and Equation (8) may be considered to define an overall mass transfer coefficient for which the driving force is the concentration of the barium in a solution of total normality c_o that is in equilibrium with the total exchanger composition. For data conforming to Equation (8), a plot of the value of the integral vs. time should result in a straight line. Figure 6 shows the experimental data plotted according to Equation (8). The lines all tend to show some slight upward curvature but may be reasonably well taken as straight lines. The mass transfer coefficients obtained from Figure 6 are included in Table 2. The *J*-factor correlation terms for these mass transfer coefficients are also given in Table 2 and are plotted on Figure 5. The diffusivity of barium ions was taken as $(0.83)(10^{-5})$ sq.cm./sec., the self-diffusivity of barium ions at infinite dilution (*21*). This value for the diffusivity was used primarily because it is the minimum possible value and therefore produces the maximum values for J_D (see subsequent discussion). Additionally, though, during almost all of the exchange process for the reverse reaction, the average barium concentration in the liquid film is much smaller than the average sodium concentration because of the unfavorable equilibrium for the sodium form of the resin and zero concentration of barium in the bulk solution. For this situation the counterdiffusion coefficient for barium tends to approach the self-diffusivity of barium (*7*).

As may be noted from Table 2, the mass transfer coefficients calculated for the reverse reaction are considerably lower at comparable flow rates than those for the forward reaction. The J-factor correlation results in a curve parallel to but much lower than that for the forward reaction despite the use of the minimum possible diffusivity in calculating the J_D's for the reverse reaction. At a given flow rate, the barium diffusivity is the only factor affecting k_L which should differ for the forward and reverse reactions. Since the maximum possible corrections for diffusivity would not be able to effect agreement between the k_L's and J_D's for the two directions, the mass transfer coefficients presented for the reverse reaction must be considered as overall coefficients, $(K_L)_{Ba}$'s and are not true film coefficients.

The low mass transfer coefficients for the reverse reaction indicate that one or more of the assumptions used to obtain Equation (8) and to evaluate film coefficients from it are inadequate. The assumption that the normalities of the bulk solution and the interface solution are essentially the same is only an approximation, though calculations based on Equations (4) and (6) and the 0.01N equilibrium curve indicate that the interface solution normality would be less than 7% higher than the bulk normality for $(\bar{q}/a)_{Ba}$ of 0.98 and less than 2% higher for $(\bar{q}/a)_{Ba}$ of 0.94. However, correcting for the increased normality of the interface solution would result in still lower mass transfer coefficients, both because some average value of the interface normality should be used in place of c_o on the right side of Equation (8) and because higher solution normalities would tend to slightly lower the equilibrium curve and thus produce higher values of the denominator in the integral. An assumption that the liquid-film mass transfer coefficient is constant is also an approximation, since this coefficient will vary during the exchange because of changes in the effective interdiffusivity of the barium ion (*16*). The exact effect of these changes is difficult to estimate; but as noted above, even with a maximum diffusivity correction by use of the self-diffusivity for barium, the J_D factors for the reverse reaction are much lower than would be expected for a true liquid-film coefficient.

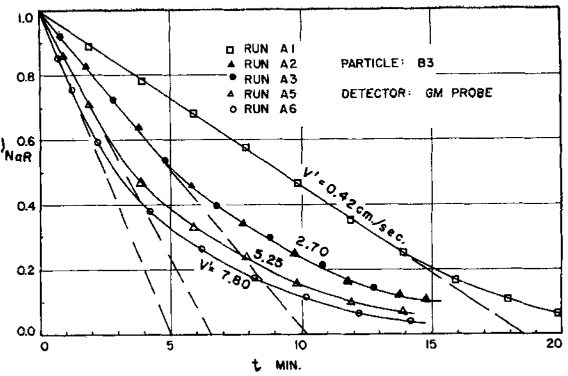

Fig. 3. Rate curves for N/100 barium chloride solution.

Internal diffusion had been considered to have no influence on the overall rate for the first portion of the reverse-reaction runs, both because of the effects of flow rate observed and because of the unimportance of internal diffusion on rate for the initial portions of the forward-reaction runs which had much higher exchange rates. It is possible, however, that the concentration gradient inside the particle, while very small, is still large enough so that even at very low fractions of sodium within the particle, the concentration of barium at the surface is slightly but discernibly lower than the average barium concentration in the particle. Because of the shape of the 0.01N equilibrium curve, this slightly lower barium concentration could cause a relatively large decrease in barium content of the interface liquid; and the true driving force for barium transfer across the liquid film would be less than that used in Equation (8). A quantitative check on this possibility was not feasible at the time of the study.

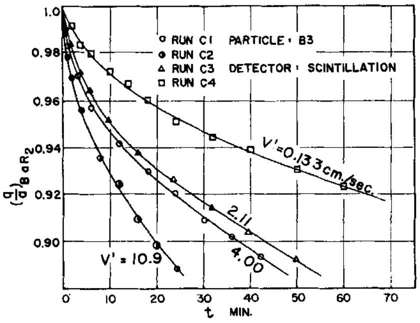

Fig. 4. Rate curves for N/100 sodium chloride solution.

The problems encountered in attempting to evaluate the liquid-film mass transfer coefficients for the reverse reaction indicate not only the difficulties possible in determining such coefficients from experimental data if the equilibrium is other than extremely favorable. They also indicate complications in the use of such liquid-film coefficients for predicting rates, complications certain of which have been overlooked in many of the theoretically based design methods proposed for ion exchange in packed beds.

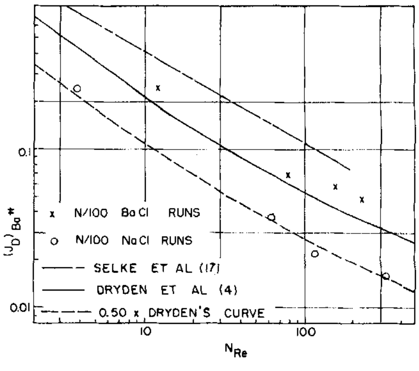

Fig. 5. Correlation of liquid-film mass transfer coefficients.

RATE STUDIES WITH 2N SOLUTIONS

In the rate studies with concentrated solutions a series of runs was made for both feed solutions with each succeeding run at a higher flow rate until the particle-saturation curve was no longer influenced by flow rate. The resulting velocity-independent curves are the internal-diffusion controlled curves for particle saturation. Figure 7 shows this curve for the reverse reaction. Figure 8 gives the experimental points for both the forward and reverse reactions, as well as for a run in which a 2N barium ion solution was passed through a bed containing a barium-charged particle, at a flow rate sufficiently high to insure internal diffusion as the controlling step. The lines in Figure 8 are calculated curves as discussed below.

Interpretation of Data in Terms of a Single-Diffusivity Model

Mass transfer within an exchanger particle has usually been treated as described by Fick's law with a constant internal diffusivity, D_i (*2, 9, 17, 19, 20*). Under the conditions of the present study (spherical particle initially saturated with one ion and with surface maintained saturated with the replacing ion starting at time $t = 0$), the fraction of the exchanger capacity in the form of the entering ion (q/a) is given by (*2, 20*)

$$\frac{q}{a} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{4n^2 \pi^2 D_i t}{d_p^2} \qquad (9)$$

A plot of this equation is furnished by the curve $D_A = D_B$ in Figure 9. The value of D_i can be obtained from such a plot by finding the values of the abscissa for several experimental values of q/a. Since the times corresponding to the q/a's selected and the particle size are known, the values of D_i can then be found for each q/a, and the average value of D_i can be determined. In general the values of D_i for each experimental curve showed good agreement among themselves and no dependence upon q/a.

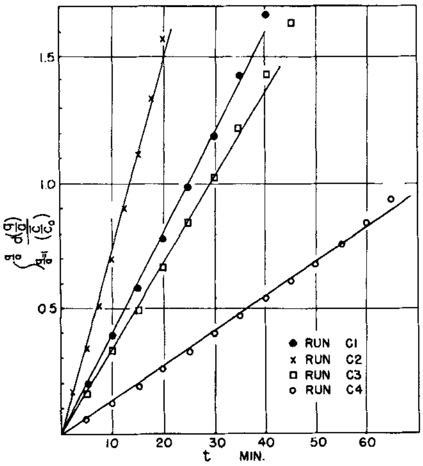

Fig. 6. Evaluation of $(K_L)_{Ba^{++}}$

The values of the internal diffusivities obtained as described above are

D_i for barium replacing sodium: $(5.24)(10^{-7})$ sq.cm./sec.

D_i for sodium replacing barium: $(1.20)(10^{-7})$ sq.cm./sec.

D_i for self-diffusion of barium: $(7.92)(10^{-8})$ sq.cm./sec.

Excellent agreement with the experimental curves was obtained by using these values to calculate particle-saturation curves (Figure 8).

Despite the satisfactory reproduction of the experimental curves with these D_i values, certain aspects of the experimental procedure introduce possibilities of error in the D_i determinations. One of these potential sources of error is the pore solution. At the start of a run, the pores of the particle contained only distilled water. During the run, anions, cations from the solution, and probably some of the displaced cations diffuse into the pores in an attempt to establish the requisite pore solution composition (see Figure 2). The exact effect of this action is difficult to evaluate, but certainly it tends to slow the removal of the displaced cations from the particle. Another potential source of error comes from the change in particle diameter with change of exchanger composition. As shown in Table 1, a maximum of 7% change of diameter occurs between the sodium and barium forms of the exchanger. An average diameter (between the sodium and barium forms) was used to compute the d_p^2 for each curve, and an error of 3% in the diameter used would produce an error of 6% in D_i.

VARIABLE DIFFUSIVITY MODEL

The self-diffusivity for sodium in the same exchanger as used in this study is given by Gopala Rao (*8*) as $(1.6)(10^{-6})$ sq.cm./sec. for exchanger in contact with 1N sodium chloride solution. The mutual internal diffusivities for the sodium-barium system lie between the self-diffusivities of sodium and barium as would be expected; but the mutual internal diffusivity for barium entering the exchanger is closer to the self-diffusivity of sodium while the mutual diffusivity for sodium replacing barium is closer to the self-diffusivity of barium. This effect is predictable if the electric forces within the exchanger, resulting from unequal ionic diffusivities, are considered (*10, 11*). Accordingly the experimental results of this study were compared with the theoretical internal diffusion curves of Plesset, Helfferich, and Franklin (*15*) which include the electrical field effects. The results are shown in Figure 9, where the subscript *A* refers to the cation initially on the exchanger. D_A/D_B is approximately 20 for the 2N barium chloride case and 1/20 for the reverse reaction. Quantitatively the agreement is fairly good for the 2N barium chloride case but rather poor for the 2N sodium chloride case. However, the pore solution effect would probably be more important for the latter case, since it is the slower process. In view of the assumptions used in the derivation of Plesset et al. (notably, no pore solution and constant value of D_A/D_B), it is felt that the experimental results from the present study strongly substantiate the importance of the electric forces on diffusion inside the ion-exchange particle.

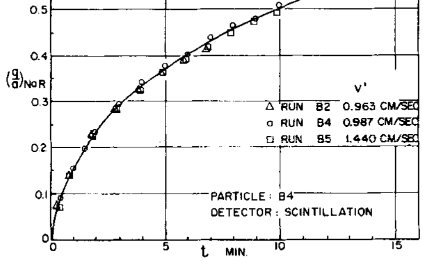

Fig. 7. Rate curve for 2N sodium chloride solution.

In light of the electric field theory and its implications, it might appear that the use of a constant internal diffusivity to represent the internal diffusion process is strictily an empirical approach, and that the good fit of the experimental data shown by the constant-diffusivity model in Figure 8 is fortuitous. However, it has been shown by Gopala Rao (8) that for the exchanger initially saturated with one ion and exchanger surface saturated with the replacing ion starting at zero time, the explicit expressions of Plesset et al. (*15*) indicate that often a constant value of the diffusivity is adequate to represent the internal-diffusion process. With the method suggested by Gopala Rao, the constant internal diffusivities for the forward and reverse reactions were estimated from the self-diffusivities of the exchanging ions to be $(4.9)(10^{-7})$ sq.cm./sec. for barium replacing sodium and $(1.5)(10^{-7})$ sq. cm./sec. for sodium replacing barium.

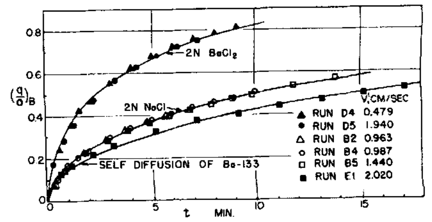

Fig. 8. Prediction of particle diffusion curves; $(q/a)_B$ refers to entering ion.

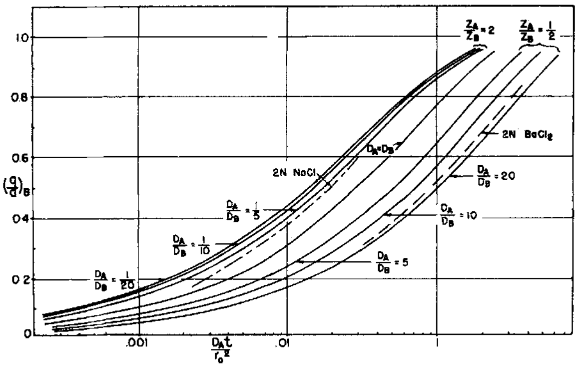

Fig. 9. Comparison of experimental data with theoretical internal diffusion curves of Plesset et al. (*15*).

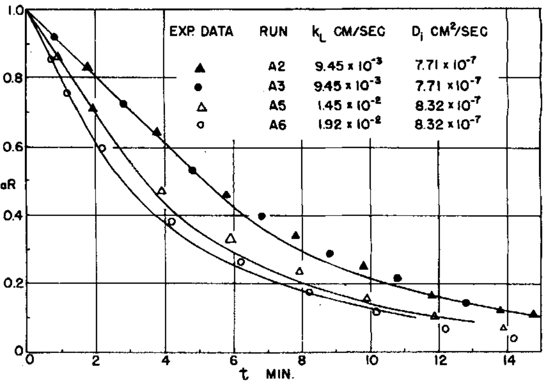

Fig. 10. Prediction of the rate curves by numerical method.

These values compare well with the experimental values previously cited of $(5.2)(10^{-7})$ and $(1.2)(10^{-7})$ sq.cm./sec. respectively.

INTERNAL AND EXTERNAL MASS TRANSFER RESISTANCES BOTH IMPORTANT

In many of the runs of the present study, the resistances to mass transfer within the particle and between the particle surface and bulk liquid were both important in determining the mass transfer rate at some portion of particle saturation. A numerical solution for such cases, programmed for the IBM-709 computer, had been established for the assumptions of no normality change in the external fluid, constant k_L and internal diffusivity, and equilibrium at the liquid-exchanger interface (*22*). This program was used to match the experimental curves for runs A2, A3, A5, and A6, for which the liquid-film mass transfer coefficients were known, by adjusting the value of the internal diffusivity until a reasonably satisfactory match was obtained. The results are shown in Figure 10, with the values of mass transfer coefficients and internal diffusivities used. The values of the internal diffusivities used agree fairly well with the D_i from the 2N study. The agreement between the predicted and experimental curves is good in view of the assumptions of the model. However, it must be noted that the liquid-film resistance, for which the mass transfer coefficient is relatively well known, controls the exchange rate for a large fraction of the curve, and the value of the internal diffusivity is chosen to produce better agreement in the latter part of the curve. It is known that the simple model used for these calculations is not generally successful (*8*), but it is of interest that the model works fairly well for this particular application.

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NOTATION

a = specific exchange capacity meq./g. of designated form, exclusive of pore solution (except for the lower 2N curve of Figure 1)
c = concentration of ion in bulk solution, meq./ml.
$\bar{c}$ = concentration of ion in solution at interface between exchanger particle and solution, meq./ml.
c_0 = total solution normality, meq./ml.
d_p = particle diameter, cm. (unless otherwise specified)
D = diffusivity of ion in water, sq. cm./sec.
D_i = diffusivity of ion inside exchanger, sq.cm./sec.
J_D = dimensionless grouping defined by Equation (4)
K = equilibrium distribution coefficient defined by Equation (2), g./ml.
k_L = mass transfer coefficient, defined by Equation (1), for transfer of an ion between bulk solution and surface of exchanger, cm./sec.
K_L = overall mass transfer coefficient, defined by Equation (8), cm./sec.
N_{Re} = Reynolds number for packed bed, defined by Equation (4)
q = concentration of ion in exchanger, meq. of ion/g. exchanger in designated form
$\bar{q}$ = concentration of ion at outer surface of exchanger; meq. of ion/g. exchanger in designated form
R = designates a monovalent exchange site of exchanger
s = external surface of exchanger, sq.cm./g. exchanger in designated form
t = time, sec.
V' = superficial velocity of liquid through bed, cm./sec.
ϵ = void fraction in packed bed
μ = liquid viscosity, poise
ρ = liquid density, g./ml.
μ eq = micro equivalent (10^{-3} meq.)

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